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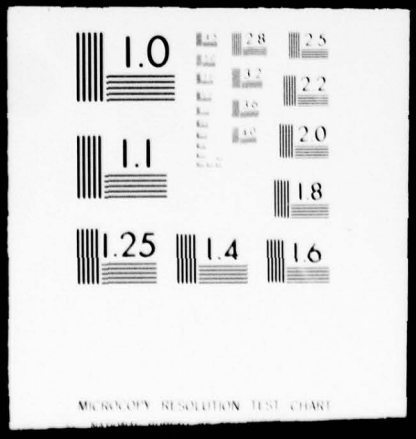

REPORT SAMSO-TR-78-134

LEVEL II

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Transient Techniques for Low Frequency Battery Impedance Measurements

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6 October 1978

Interim Report

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This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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A general formalism is developed for obtaining battery impedances as a function of frequency from the time response to an input current step. As an example, this technique is applied to impedance measurements for a 10-ampere hour nickel cadmium satellite cell. The impedance over the frequency range of 0.5 Hz to 10^{-6} Hz is indicative of diffusion controlled cell polarization.

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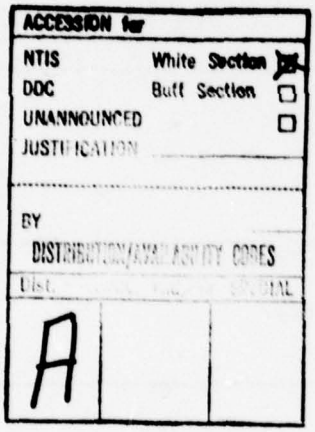
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FIGURES

I. INTRODUCTION

The electrical impedance of a chemical system over a broad frequency range provides an important source of information on the rates and mechanisms of electrochemical reactions as well as the physical properties of conducting media. In recent years, impedance measurements have been particularly useful as probes of dynamic behavior in electrochemistry,[1-4] solid state technology,[5,6] and corrosion chemistry.[7,8] However, very little work has been done utilizing broadband impedance measurements to study the kinetics of processes occurring in practical battery systems. This situation arises from experimental difficulties related to the extremely low impedances typical of battery cells, as much as from the intrinsic chemical and physical complexity of the cell system. However, recent applications of broadband impedance studies to LeClanche cells,[9] lead-acid cells,[10,11] and nickel cadmium button cells[12] point out the usefulness of impedance characterization for studying cell properties.

Traditionally, the impedance of an electrochemical system is obtained for a sinusoidal steady state at a particular frequency from the amplitude and phase relations between the current and voltage. However, with recent technological advances in computerization and digital processing, it is becoming more common for impedances to be measured using Fourier transform[8,13] or transient[14,15] techniques. These techniques employ transform methods to obtain the impedance from the time dependent response of the system to pink or white noise[8] or a transient stimulus.[15] Transient

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techniques in particular are expected to offer noteworthy advantages over classical alternating current methods in terms of application to battery cell measurements.

Foremost among these advantages is the applicability of transient techniques to arbitrarily low frequency measurements. This is particularly useful in studying the kinetics and properties of high capacity storage cells where extremely slow diffusion processes are often important. Furthermore, a single transient measurement allows the impedance to be obtained at all frequencies represented in the experimental time domain response of the system under investigation. At low frequencies in particular, this results in significantly less time being required for experimental measurements than in the case of alternating current methods, where separate impedance measurements must be made at each frequency of interest. Finally, problems due to changes in the state of a cell arising from charge or discharge during the course of a measurement may, in special cases, be treated explicitly for transient methods.

In this report we present a general theoretical and experimental formalism for the application of transient impedance measurements to battery cells. Much of the formalism is based on relatively well understood transform methods,[16] and therefore will only be treated briefly. However, a detailed treatment of the application of these methods to measurements on electrochemical energy systems will be presented.

II. FORMALISM

If a time dependent stimulus e(t) is applied to a system, the impedance of the system to this stimulus is given by

$$z(t) = e(t) / i(t), \tag{1}$$

where i(t) is the response of the system to the stimulus. For an electrical system, the stimulus and response are typically the voltage and current. Using Eq. 1, a time dependent impedance may be determined from voltage and current transients. However, it is usually more convenient to study the impedance as a function of frequency rather than time. This is accomplished by transforming the stimulus and response functions from the time domain to the frequency domain, whereupon their ratio gives the frequency dependent impedance.

$$Z(\omega) = E(\omega) / I(\omega). \tag{2}$$

The transformation of a time dependent function f(t), to the frequency domain may be done by means of the Laplace transformation.

$$F(\omega) = \int_0^\infty f(t) \exp(-j\omega t)\, dt. \tag{3}$$

Using Equation 2, the impedance of battery cells may be determined by applying a current or potential step to the cell, and observing the resultant time dependent voltage or current respectively. Battery cells typically behave like large capacitors at low frequencies, and therefore it is most convenient at low frequencies to control the current and observe the voltage change resulting from a current step. The impedance obtained from the system response to a current step generally differs from the impedance obtained at a sinusoidal steady state. In the case of a battery cell, the impedance will, in general, vary with the direction of current flow. The impedance for a charging current will not be the same as that for a discharge current unless the processes controlling these impedances are reversible. In the reversible case, galvanostatic transient impedances are equivalent to the alternating current impedance.

Processes related to diffusion often occur quite slowly in battery cells, and therefore voltage transients must be monitored for periods of time up to several hours. In this case, the cell will be somewhat charged or discharged during the measurement, and a natural voltage change arising from the chemical changes associated with energy storage or dissipation will appear superimposed on the time dependent voltage of the cell. The cell voltage may be separated into the natural behavior $e_N(t)$, and the transient behavior $e_t(t)$, provided the current step perturbs the state of the cell only slightly.[17]

$$e(t) = e_N(t) + e_t(t). \tag{4}$$

We furthermore assume that for a small perturbation the natural behavior is linear with time, an assumption which is expected to be quite good for capacity changes of less than 1% of the remaining cell capacity. Eq. 4 now may be written

$$e(t) = e_t(t) + Ct + D \tag{5}$$

where C and D are constants describing the natural cell response, and will vary with current, state of charge, temperature, and direction of current flow.

The transient impedance may be expressed in terms of the time dependent voltage $e_t(t)$ obtained when a current step I_o, is applied to the cell.

$$Z_t(\omega) = E_t(\omega)/I(\omega) = \frac{j\omega}{I_o}\int_0^\infty e_t(t)\,\exp(-j\omega t)\,dt, \tag{6}$$

where I_o is the negative for discharge and positive for charging currents. For example, a typical transient response of a cell to a small discharge

current is illustrated in Figure 1. From this figure it may be seen that

$$e_t(t) = e(t) - (E_o + e_N(t)) \tag{7}$$

where E_o is a positive constant. The instantaneous change in $e_t(t)$ at zero time represents the frequency independent resistive component of the impedance.

The Laplace transform in Eq. 6 may be evaluated numerically by assuming exponential behavior for $e_t(t)$ between successive data points.

$$\int_o^\infty e_t(t) \exp(-j\omega t)\, dt = \sum_i \frac{e(t_i)}{\exp(-at_i)} \int_{t_i}^{t_{i+1}} \exp\left[-t(a + j\omega)\right] dt, \tag{8}$$

where

$$a = \frac{\ln\left[e(t_{i+1})/e(t_i)\right]}{t_i - t_{i+1}} \tag{9}$$

and it is assumed that in the interval between t_i and t_{i+1}, $e_t(t)$ may be represented by an exponential,

$$e_t(t_i) = B_i \exp(-at_i). \tag{10}$$

This assumption, of course, requires that the sampling interval be made sufficiently small. Equation 8 may be evaluated to give

$$E_t(\omega) = \sum_i \frac{B_i}{a + j\omega} \left[\exp(-t_i(a + j\omega)) - \exp(-t_{i+1}(a + j\omega))\right]. \tag{11}$$

From this expression and the magnitude of the current, Equation 6 may be used to evaluate the impedance at all frequencies for which adequate time domain sampling of the voltage and current is available. This sampling rate is primarily determined by the time interval over which the system response may be closely approximated by an exponential.

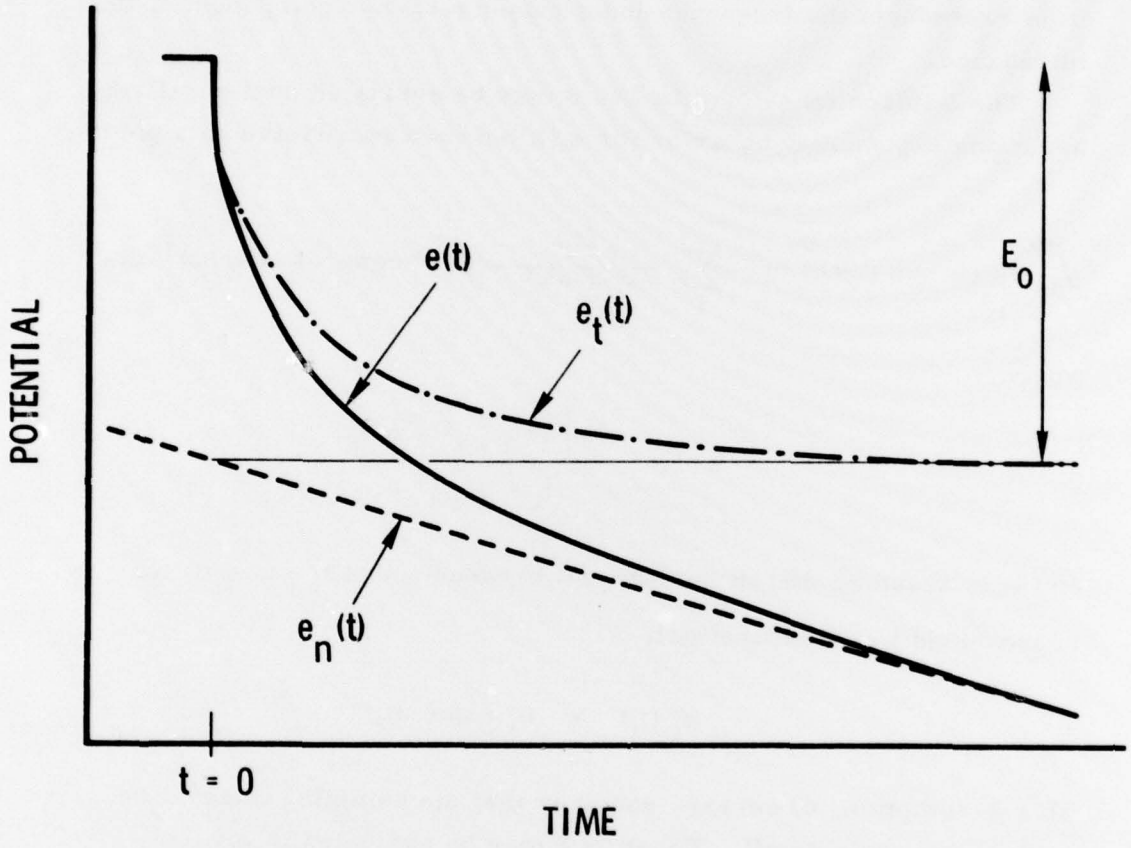

Fig. 1. Illustration of a Typical Voltage Response of a Cell to a Step Discharge Current Initiated at Zero Time. The overall voltage response is e(t) (–), and is comprised of the Natural response $e_N(t)$ (----) and the transient response $e_t(t)$ (– · – · –).

III. EXPERIMENTAL

A brief outline of the experimental method employed for low frequency impedance measurements will be presented here, and some experimental data for a 10 ampere-hour nickel cadmium cell will be presented. Experimentally, it is most convenient to control current rather than voltage for battery cells, therefore a current step function was applied to the battery cell and the voltage response function was measured. Figure 2 presents a block diagram of the experimental apparatus used in making these measurements.

Important features of the experimental apparatus in Figure 2 are the requirements that the temperature of both the cell and the offset voltage have a long term stability of about $\pm 0.01^{\circ}C$. This is necessary because nickel cadmium cells have rather large temperature coefficients[18] ($-0.5\ mV/^{\circ}C$), and the offset voltage batteries and resistors also have substantial temperature coefficients. The chopper-stabilized amplifier must have high thermal stability ($0.5\ \mu V/^{\circ}C$) and drift of less than $1\ \mu V$ per day. Since we are primarily concerned here with frequencies of less than 1 Hz, a standard toggle switch was used to initiate a discharge current of about 1 mA for a 10 ampere hour nickel cadmium satellite cell. The voltage response was recorded at an overall sensitivity of $10\ \mu V$ per inch, with a time resolution of about 0.2 sec. The impedance at frequencies higher than roughly 0.1 to 0.5 Hz was therefore not obtained, but could be measured by using a high speed switch, a high speed amplifier, and measuring the fast current and voltage time responses on an oscilloscope.

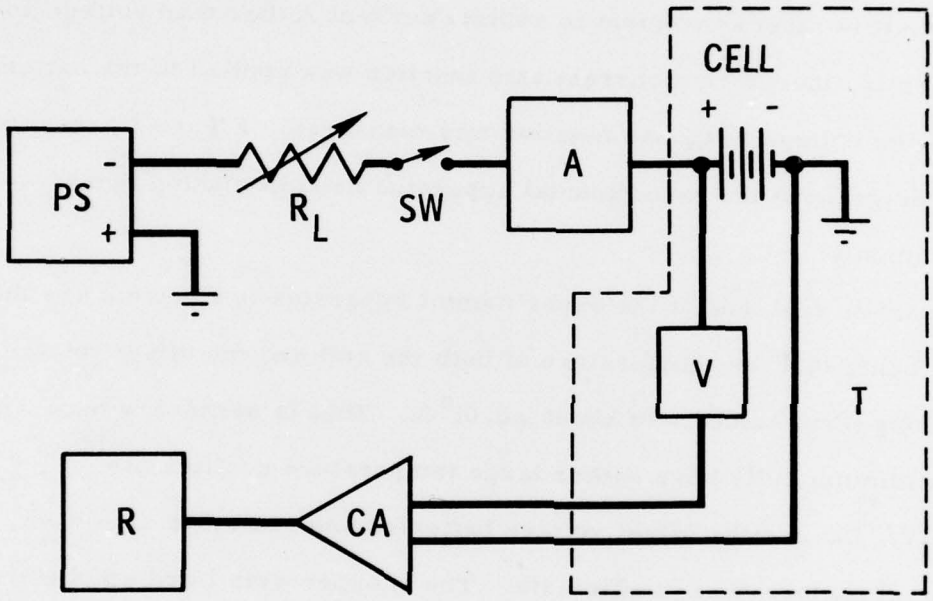

Fig. 2. Apparatus Used for Measuring the Voltage Response of a Battery Cell to a Current Step Function. PS is a 10 volt power supply, R_L a variable load resistor, SW is the switch for turning on the current step, A a milliammeter, V is a voltage offset, CA a low drift chopper-stabilized amplifier, R is a recorder; the dashed line encloses T, the constant temperature bath regulated to ±0.01° C drift per day.

The cell being studied was discharged at 1.113 mA for about 5 hours before its voltage assumed a linear decrease with discharge. The cell capacity discharged during this experiment was about 0.005 ampere hours, or 0.05% of the cell capacity. A linear natural response is assured over this small change in the cell state of charge. The voltage response of the nickel cadmium cell is shown in Figure 3 for a 1.113 mA discharge current at 25.05°C. The cell voltage decreased a total of 1.236 mV during the course of this experiment. The transient cell response, $e_t(t)$ in Equation 7, accounted for 0.651 mV of this decrease, while the remainder was attributed to the natural cell response. The Laplace transform of the transient voltage response in Figure 3 may be used in Equation 6 along with the magnitude of the discharge current, to give the cell impedance as a function of frequency. The cell impedance is presented in Figure 4 using a Cole-Cole plot of resistive vs. reactive impedance components at each frequency. In this type of plot, the frequency spectrum sweeps out a curve which is characteristic of the electrical properties of the system.

The impedance from 10^{-6} to 0.1 Hz was obtained from the data in Figure 3 using the transient method outlined in this report. For comparison, the impedance from 10 Hz to 200 KHz was obtained using a standard alternating current method employing a gain-phase meter.[11] The frequency dependence of the impedance determined by these two methods is in agreement, showing a smooth transition from a high frequency inductive region to capacitive behavior at low frequencies. This agreement shows that these two techniques for measuring impedance are complementary, each being particularly well suited to a specific frequency regime. The overall frequency dependence shown in Figure 4 may be qualitatively interpreted in terms of the cell properties. At high frequencies a net self inductance

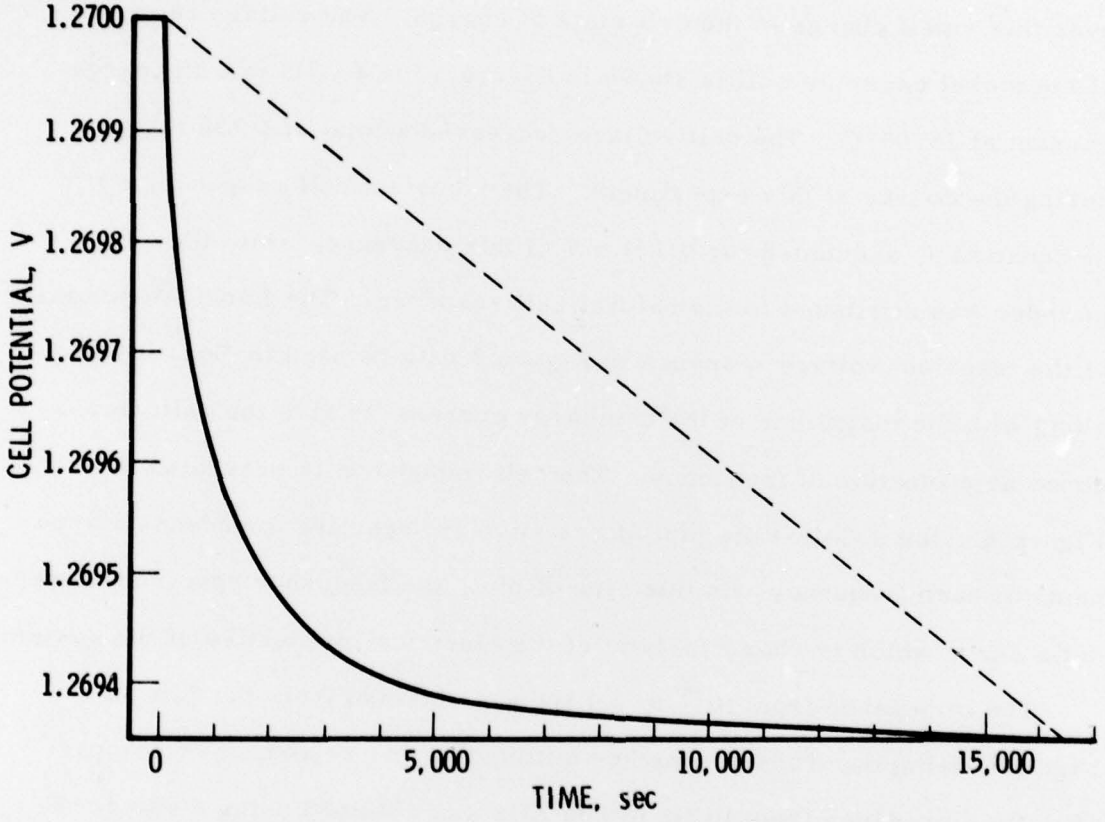

Fig. 3. Transient Potential Response $e_t(t)$ (—) of Nickel Cadmium Cell L1-137 for a 1.113 mA Discharge Current Applied at Zero Time. The cell is about 60% charged and the temperature is 25.05 ± 0.01°C. The natural cell response to this discharge current is given by the dashed line (----).

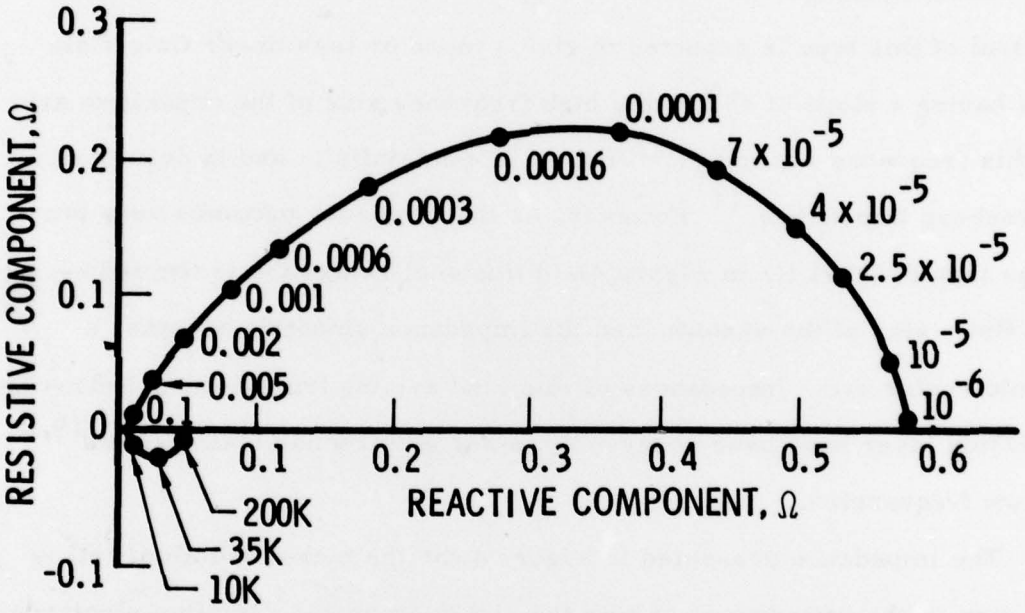

Fig. 4. The Impedance of Nickel Cadmium Cell L1-137 at 25.05°C and a State of Charge of About 60%. The impedance from 10^{-6} to 0.1 Hz was obtained from the voltage transient of Figure 3, while from 10 Hz to 200 KHz it was obtained using an alternating current method.

results from the structure of the porous electrodes. This type of self inductance has previously been discussed in relation to lead-acid cells [11] and nickel cadmium cells.[12] It is expected to be quite significant for sintered plaque electrodes such as those in nickel cadmium cells, and should show little change with state of charge. At low frequencies a skewed capacitive arc is observed. This behavior is consistent with an impedance arising from a diffusion layer of finite thickness. Diffusion control of this type is expected to give a more or less linear Cole-Cole plot having a slope of 45° on the high frequency side of the capacitive arc. In this frequency regime the diffusion is semi-infinite and is described as a Warburg impedance.[14] However, as the frequency becomes very low (less than 0.00001 Hz in Figure 4), diffusional relaxation is limited by the finite size of the system, and the impedance smoothly becomes a semicircular arc. Impedances of this kind arising from a finite Nernstian diffusion layer have been observed in other electrochemical systems[19, 20] at low frequencies.

The impedance presented in Figure 4 for the nickel cadmium cell is the sum of the impedances of both the nickel oxide and cadmium electrodes, and since the relaxation rates of the processes at each of these electrodes are likely to be different, deviations from the ideal behavior outlined in the previous paragraph are likely to occur. These deviations are exhibited in the experimental data of Figure 4 as a noticeable curvature in the impedance plot between 0.1 and 0.0005 Hz, whereas a straight line having a slope of 45° is ideally expected assuming that finite plane diffusion is the predominant controlling process. Impedance measurements for a single electrode should simplify data such as that in Figure 4, however, such measurements involve the use of a third electrode for reference

purposes, and therefore require special cell construction. It is also likely that the low frequency impedance depends on current and temperature, as well as state of charge. Such effects remain to be investigated.

A key assumption which we have made in the transient method which has been presented is that the natural and transient cell responses are independent of each other as expressed by Equation 7. The natural response is primarily due to the overall changes in electrolyte and electrode activities associated with the electrochemical charge or discharge reaction, while the transient response arises primarily from changes in local concentration and double-layer characteristics at the electrode interface. It is reasonable that the resultant small changes in electrolyte concentration (which arise from the extremely low discharge current) will have little effect on diffusional and interfacial properties. In addition, a linear natural response is assured by the extremely small perturbation to which the cell is subjected by the low discharge current.

The upper frequency limit of 0.1 Hz on the impedance obtained from the data in Figure 3 results from the time constant of the data recording system, and could be easily improved to about 10 KHz with the use of a high speed amplifier and an oscilloscope or microprocessor for data acquisition. A microprocessor system is currently being obtained for these measurements.

IV. CONCLUSIONS

A technique has been developed which is well suited for very low frequency impedance measurements on battery systems. Impedances at frequencies from 10^{-6} to 0.1 Hz may be measured without specialized equipment, and if a microprocessor data acquisition system is available,

frequencies up to 10 KHz are easily accessible. These measurements appear to offer a useful approach to the study of slow chemical and physical processes in battery cells, as well as the relationships of these processes to cell performance characteristics.

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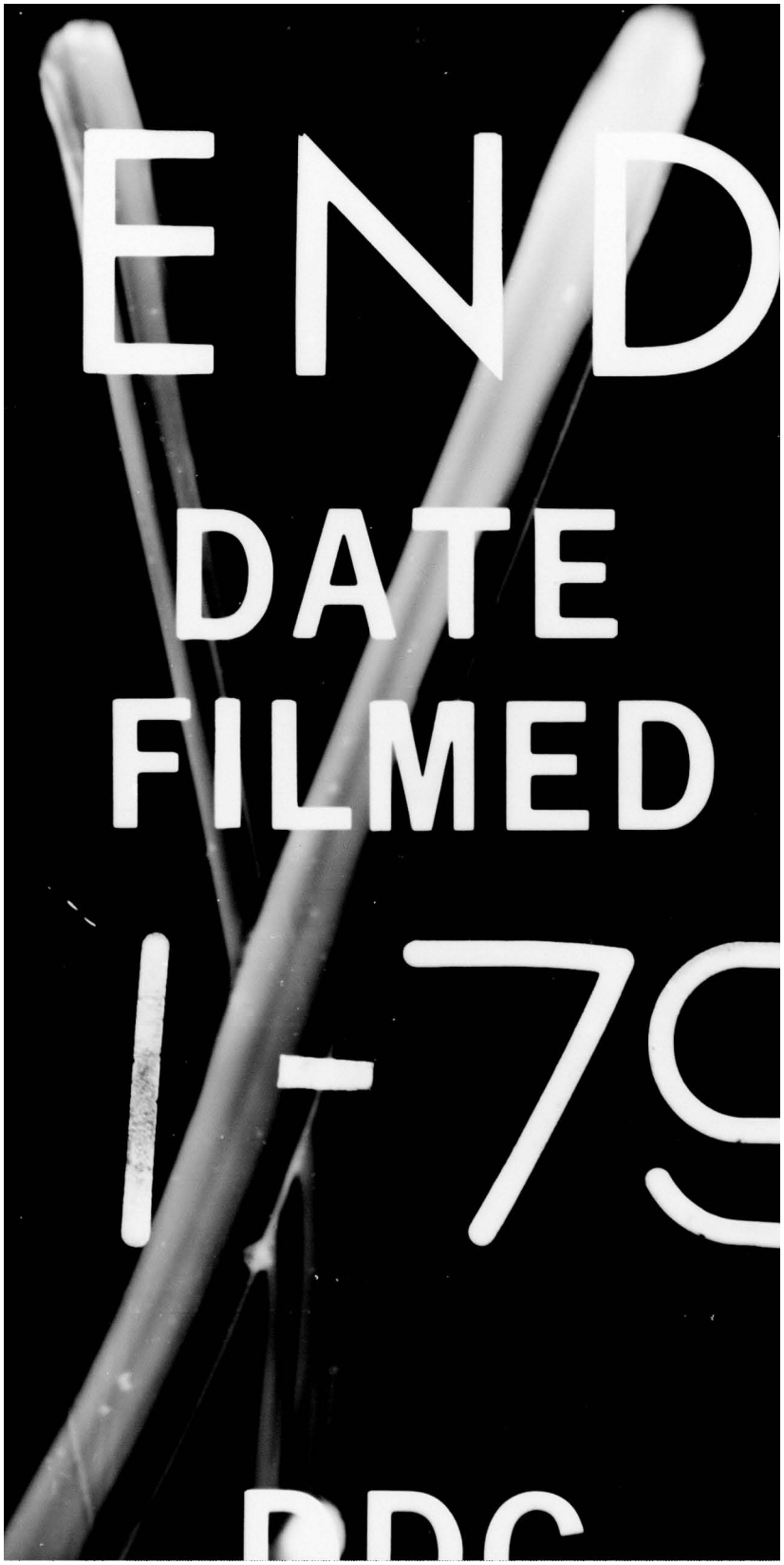
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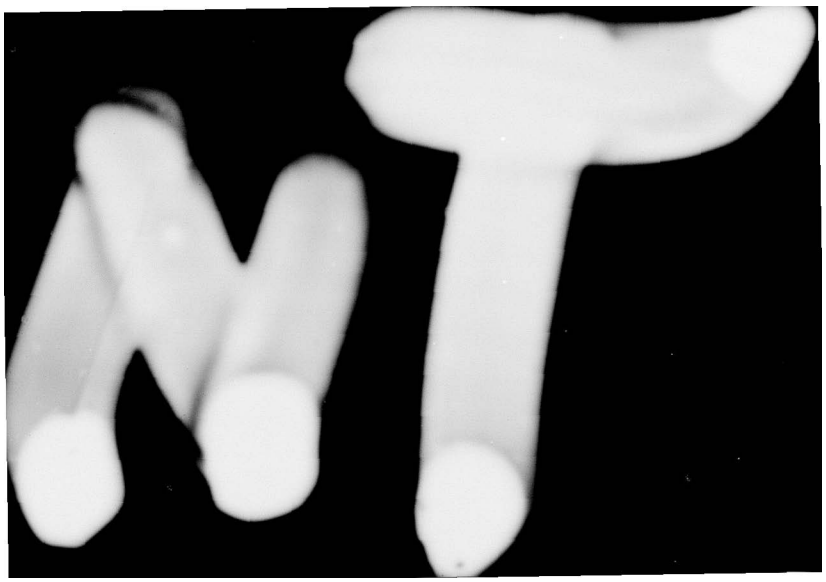
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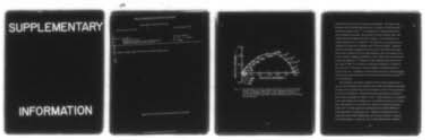

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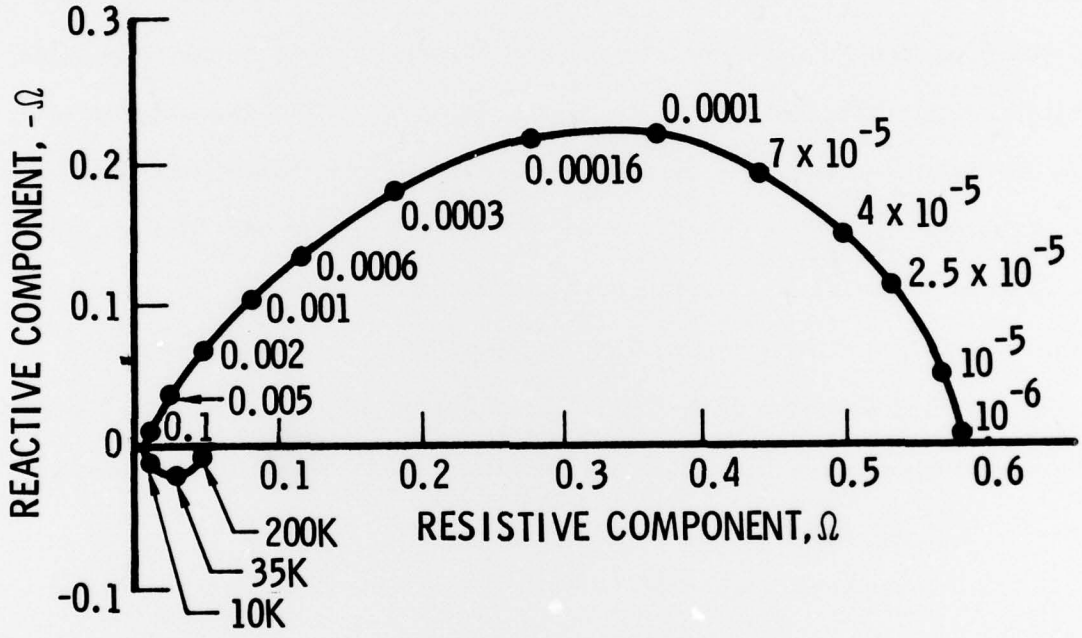

Fig. 4. The Impedance of Nickel Cadmium Cell L1-137 at 25.05°C and a State of Charge of About 60%. The impedance from 10^{-6} to 0.1 Hz was obtained from the voltage transient of Figure 3, while from 10 Hz to 200 KHz it was obtained using an alternating current method.

results from the structure of the porous electrodes. This type of self inductance has previously been discussed in relation to lead-acid cells [11] and nickel cadmium cells.[12] It is expected to be quite significant for sintered plaque electrodes such as those in nickel cadmium cells, and should show little change with state of charge. At low frequencies a skewed capacitive arc is observed. This behavior is consistent with an impedance arising from a diffusion layer of finite thickness. Diffusion control of this type is expected to give a more or less linear Cole-Cole plot having a slope of 45° on the high frequency side of the capacitive arc. In this frequency regime the diffusion is semi-infinite and is described as a Warburg impedance.[14] However, as the frequency becomes very low (less than 0.00001 Hz in Figure 4), diffusional relaxation is limited by the finite size of the system, and the impedance smoothly becomes a semicircular arc. Impedances of this kind arising from a finite Nernstian diffusion layer have been observed in other electrochemical systems[19, 20] at low frequencies.

The impedance presented in Figure 4 for the nickel cadmium cell is the sum of the impedances of both the nickel oxide and cadmium electrodes, and since the relaxation rates of the processes at each of these electrodes are likely to be different, deviations from the ideal behavior outlined in the previous paragraph are likely to occur. These deviations are exhibited in the experimental data of Figure 4 as a noticeable curvature in the impedance plot between 0.1 and 0.0005 Hz, whereas a straight line having a slope of 45° is ideally expected assuming that finite plane diffusion is the predominant controlling process. Impedance measurements for a single electrode should simplify data such as that in Figure 4. however, such measurements involve the use of a third electrode for reference